

Ames $^{32}\text{S}^{16}\text{O}^{18}\text{O}$ Line List for High-Resolution Experimental IR Analysis

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Abstract

By comparing to the most recent experimental data and spectra of the SO₂ 628 ν_1/ν_3 bands (see Ulenikov *et al.* JQSRT 2016, 168, 29-39), this study illustrates the reliability and accuracy of the Ames-296K SO₂ line list, which is accurate enough to facilitate such high-resolution spectroscopic analysis. The SO₂ 628 IR line list is computed on a recently improved potential energy surface (PES) refinement, denoted Ames-Pre2, and the published purely *ab initio* CCSD(T)/aug-cc-pVQZ dipole moment surface. Progress has been made in both energy level convergence and rovibrational quantum number assignments agreeing with laboratory analysis models. The accuracy of the computed 628 energy levels and line list is similar to what has been achieved and reported for SO₂ 626 and 646, i.e. 0.01 – 0.03 cm⁻¹ for bands up to 5500 cm⁻¹. During the comparison, we found some discrepancies in addition to overall good agreements. The three-IR-list based feature-by-feature analysis in a 0.25 cm⁻¹ spectral window clearly demonstrates the power of the current Ames line lists with new assignments, correction of some errors, and intensity contributions from varied sources including other isotopologues. We are inclined to attribute part of detected discrepancies to an incomplete experimental analysis and missing intensity in the model. With complete line position, intensity, and rovibrational quantum numbers determined at 296K, spectroscopic analysis is significantly facilitated especially for a spectral range exhibiting such an unusually high density of lines. The computed 628 rovibrational levels and line list are accurate enough to provide alternatives for the missing bands or suspicious assignments, as well as helpful to identify these isotopologues in various celestial environments. The next step will be to revisit the SO₂ 828 and 646 spectral analyses.

I. Introduction

Recently the ν_1 and ν_3 high-resolution spectra of $^{16}\text{O}^{32}\text{S}^{18}\text{O}$, denoted SO_2 628, has been measured in laboratory experiments and reported in Ulenikov *et al.*[1] It is the first high resolution rovibrational spectrum reported for an asymmetric isotopologue of SO_2 . The FT-IR measurements were carried out in the $930 - 1580 \text{ cm}^{-1}$ range using a Bruker IFS120 FTIR spectrometer, on the mixed sample of $^{16}\text{O}^{32}\text{S}^{16}\text{O}$ (626), $^{18}\text{O}^{32}\text{S}^{18}\text{O}$ (828) and $^{16}\text{O}^{32}\text{S}^{18}\text{O}$ (628) formed by allowing $^{32}\text{S}^{18}\text{O}_2$ to exchange O atoms with H_2O gas. The 628 ratio was estimated between 30% and 40% during the second half of the 30-hour measurement. The total line width was $0.0024 - 0.0028 \text{ cm}^{-1}$ at 298K. Their fitted spectroscopic Hamiltonian model terms can reproduce 81 $\nu_1 \leftarrow \nu_1$ and $\nu_3 \leftarrow \nu_3$ microwave frequencies to $\sigma_{\text{RMS}} = 0.16 \text{ MHz}$.

In 2014 and 2015, we published the Ames-296K IR line lists for SO_2 symmetric isotopologues, including the main 626 and minor 646,636,666 and 828.[2,3] They cover from the ground state to an upper state energy $E' = 8000 \text{ cm}^{-1}$, and J up to 70-80, with intensity cutoff of $1\text{E-}36 \text{ cm/molecule}$. The Ames-296K lists are based on exact quantum rovibrational calculations within the Bohn-Oppenheimer approximation using a CCSD(T)/aug-cc-pV(Q+d)Z dipole moment surface and a potential energy surface (PES) refined with selected high-resolution experimental data. The SO_2 626 rovibrational energy levels included in our refinement were selected from HITRAN2008 [4] data (with $\text{ierr} \geq 4$) at $J=0/4/20/50/70$. Note the SO_2 data collection in HITRAN2012 [5] is the same as in HITRAN2008. This “Best Theory + Reliable High-Resolution Experimental Data” strategy has led to the most reliable predictions including (but not limited to) missing band interpolations, higher energy band extrapolations, and extrapolations to other minor isotopologues, as we have also found for NH_3 [6,7,8,9] and CO_2 [10,11,12]. The Ames-1 PES refinement did not include any recent experimental measurements after 2008, but the accuracy and reliability of the Ames-296K line list predictions have been confirmed several times. Most comparisons between our lists and Ulenikov group’s studies [13,14,15,16,17,18,19] have satisfactory agreement. For strong transitions, the relative intensity ratios are comparable between calculations and reported transmittances or spectra, with agreement better than 85-90%. At the higher wavenumber range or higher K_a , the prediction accuracy and agreement degrades slowly but systematically. All main features in

the newly recorded spectra [13-19] by the Ulenikov group match our predictions to within $\pm 0.02 \text{ cm}^{-1}$ and $\pm 10\%$ for line position and intensity, respectively. This agreement actually confirms the accuracy and reliability of the Ames-296K predictions. For example, in 2013 the new H_{eff} model published by the Ulenikov group for SO_2 626 had resolved the discrepancies on the ground state high K_a levels ($K_a > 30$) by including higher K_a experimental data. The new H_{eff} model directly verified that our Ames-1 PES based line lists provides more consistent and reliable predictions than the old HITRAN [4,5] / CDMS [20] model for those $K_a > 33-35$ levels and transitions.

Therefore, it is quite interesting when we have identified lines in both very good agreement and obvious discrepancies when compared to this latest SO_2 628 work. There also exists unique features in both the experimental analysis and our theoretical calculations for this asymmetric isotopologue. Currently we are working on the next generation of PES refinement, i.e. Ames-2, which we expect to finish in 2016. The difference between the new PES and line lists mainly lies in higher energy region of overtones and combination bands, while the ground state, v_1 and v_3 part of the PES and line list are essentially the same as the published Ames-1 PES (with stretching mode basis bug fixed, see Ref.3). This paper presents details of a comparison between the latest Ames-296K list and Ulenikov group's SO_2 628 work, plus CDMS data. The basic conclusions we reach here are that our line list predictions are still accurate and reliable enough to assist experimental IR analysis and identify errors in existing assignments or models, for 628 and other SO_2 asymmetric isotopologues.

The paper is organized as follows: Section 2 give a simple summary on the Ames-1 PES, Ames-296K line list, on-going Ames-2 PES refinement, and properties of the line list and energy levels used in the comparison. Section 3 “Results and Discussions” has four subsections. First subsection compares to data in CDMS. Second and third subsections compare to the new v_1 and v_3 spectra, including general comparison, statistics, and specific transitions where discrepancies have been identified. A special fourth subsection is devoted to the features contained in the 0.25 cm^{-1} window (Fig.2, Ref.1) where the mixings from both 626 and 828 need to be treated together. A summary and conclusions are given in Section 4.

Note that more papers have appeared from the same experimental group after Ref.1, including Ref.21-22 on 828, and Ref.23 on 646. Comparison and predictions will be discussed in separate papers (in

preparation).

II. Technical Details

Most basics of the Ames-1 PES empirical refinement algorithm and published Ames-296K lists for the five symmetric isotopologues have been reported, so a short summary is given below. Interested readers please refer to Ref.2 and Ref.3 for more details.

A CCSD(T)/cc-pVQZ-DK based PES was chosen for empirical refinement and the refined PES was denoted Ames-1. As pointed out in Ref.3, an internal parameter adopted in our variational rovibrational program (VTET) [24] was not set to a completely converged value, in both pre- and post-refinement computations of $^{32}\text{S}^{16}\text{O}_2$. This defect did not affect the energy levels and transition intensities we computed for those symmetric isotopologues, as long as the same parameter is used in all VTET calculations. The previously reported band origins and Ames-296K line list of $^{32}\text{S}^{16}\text{O}_2$ are still accurate to the limits we have quoted (i.e. to $\sigma_{\text{rms}} = 0.015 \sim 0.020 \text{ cm}^{-1}$ for rovibrational levels) But other variational programs running with the originally reported Ames-1 PES will not get the exact same energies. Certain band origins may have deviations as large as $0.1 - 0.2 \text{ cm}^{-1}$. The defect has been fixed and a new Ames-1 PES, denoted Ames-1B, has been shared with colleagues [Ref.25] and used in Ames local calculations.

In Ref.3, the new Ames-1B PES was not explicitly discussed because the old Ames-1 based results carry the essentially same accuracy. However, for the asymmetric isotopologues, e.g. 628, the old potential expansion basis defect had an impact on $J=0$ vibrational fundamentals, on the order of $\sim 0.1 \text{ cm}^{-1}$. This required us to use the Ames-1B PES or do further refinement to get a new PES. We have chosen to do the next cycle of PES refinement and line list computations. As we stated before, the “Best theory + High-resolution Experimental Data” strategy is a process in which both experimentalists and theoreticians can mutually benefit from it. Our predictions, including interpolations and extrapolations, can facilitate experimental spectrum analysis to reach higher energy, higher vibrational quantum number, or higher J/K_a . The new experimental data acquired in laboratory experiments will further guide our refinement procedure towards a better prediction accuracy and reliability in the further extrapolated region. A good example can be found in our NH_3 studies.[Ref.9] For SO_2 , our Ames-1 (and Ames-1B) refinement is fully based on

selected HITRAN[5]/CDMS[20] SO_2 626 data. Since then, there have been no SO_2 updates for HITRAN or CDMS. We believe it is time to include most new experimental data that the Ulenikov group has reported since 2008 [Refs.13-19,21]. Additional SO_2 646 data kindly shared by Dr. Flaud [26] are included as well as other 646 data reported elsewhere.[27,28,29] The new refinement is nearly complete and the prediction reliability of several potential Ames-2 candidate refinements is being studied.

For this paper, the differences between those varied PES refinements are nearly 100% negligible in the v_1 and v_3 region. We are very confident with the current SO_2 628 line list computed on a PES candidate, denoted as Ames-Pre2. Table 1 lists the three vibrational fundamentals computed on the Ames-1, Ames-1B and Ames-Pre2 PESs. Note we have included the $5v_1$ overtone for which 626 experimental data is available.[30] For 626, the Ames-1B PES gives the best agreement for $5v_1$, and both Ames-1 and Ames-Pre2 values are higher by $\sim 0.1 \text{ cm}^{-1}$. We may want to work further on this $5v_1$ aspect, but also to maintain the accuracy for all other states below that. An Ames-2 PES will be reported in due course, probably in a paper in preparation for the SO_2 828 and 627 isotopologues.

The basic conclusions to be drawn from Table 1 are: (1) the Ames-1 defect leads to $\sim 0.1 \text{ cm}^{-1}$ deviations on the asymmetric stretch fundamentals of SO_2 628 / 627; (2) the latest Ames-Pre2 PES has $\leq 0.02 \text{ cm}^{-1}$ deviations for SO_2 628 v_1 and v_3 ; (3) the Ames-1B performance for 628 v_1 and v_3 is slightly better than Ames-Pre2. The $0.004 - 0.008 \text{ cm}^{-1}$ differences between Ames-1B and Ames-Pre2 can be safely ignored, and Ames-Pre2 works as well as Ames-1B for the 628 related comparisons in this paper.

Table 1. Vibrational fundamentals of 5 SO_2 isotopologues computed using the Ames-1, Ames-1B and the latest Ames-Pre2 PESs, compared to available experiments.

	v_1	v_2	v_3	$5v_1$
626				
Ames-1	1151.71155	517.87083	1362.05856	5682.26724
Ames-1B	1151.71382	517.87249	1362.05488	5682.17391*
Ames-Pre2	1151.70929	517.87258	1362.04648	5682.27446
Expt	1151.7130 [31]	517.8726 [32]	1362.0603 [31]	5682.1692 [30]
646				
Ames-1	1144.4881	513.5337	1345.08275	5647.5290
Ames-1B	1144.48729	513.53630	1345.08855	5647.41368
Ames-Pre2	1144.47592	513.53419	1345.07982	5647.51496
EXPT [28]	1144.47863	513.53871	1345.09464	
828				

Ames-1	N/A	N/A	N/A	N/A
Ames-1B	1101.13115	496.60618	1318.53466	5435.24845
Ames-Pre2	1101.13765	496.60541	1318.51958	5435.34016
EXPT [21]	1101.13648(3)		1318.54800(3)	
628				
Ames-1	1123.90994	507.37303	1342.68917	5543.83484
Ames-1B	1123.91688	507.36866	1342.80265	5543.79261
Ame-sPre2	1123.91292	507.36830	1342.79414	5543.90204
EXPT [1]	1123.930266(91)		1342.812057(94)	
627				
Ames-1	1137.77914	512.37052	1351.23491	5613.20958
Ames-1B	1137.72439	512.35916	1351.30677	5613.07476
Ames-Pre2	1137.71997	512.35897	1351.29832	5613.18002

The dipole moment surface (DMS) used in our line list calculations is purely *ab initio*. It was fit from CCSD(T)/aug-cc-pV(Q+d)Z finite-field dipole calculations on nearly three thousand geometries, with higher weights focused on $E' < 30,000 \text{ cm}^{-1}$. The average fitting error and average relative error are $1.8 \times 10^{-5} \text{ a.u.}$ and 0.010 %, respectively. This DMS fitting accuracy should be enough to ensure the reliability of intensity predictions on the strong v_1 and v_3 bands. All previous comparisons [2,3] have confirmed this. The agreement is better for minor isotopologues, for which we believe less H_{eff} -based extrapolations have been included in HITRAN [5] and CDMS [20] data.

Rovibrational energy levels, wave functions, and transition intensity calculations were all carried out with the VTET program as described in Ref.2. We have been using the same energy cutoffs: 0.187 Hartree for solving the one-dimensional stretching Schrödinger equations and later fully contracted basis functions, i.e. 41042 cm^{-1} (1 Hartree = $219,474.6 \text{ cm}^{-1}$). 0.055 Hartree (12071 cm^{-1}) for the roots. In our last paper,[3] a few cases of slowly converging energy levels and intensities have been identified and we have increased the maximum rotational quantum number from 240 to 360, and the number of quadrature points for the angular part of integrals from 180-200 to 220-240. These upgrades were found critical for having a smooth and complete $J=0-80$ based line list at 296K for each isotopologue. However, for 628, these improvements are not enough.

Convergence Improvement

One of the most difficult part of SO_2 628 calculations is the resonance affected $K_a=0/1$ levels at higher

J (e.g. $J > 50$). Sometimes it requires unusually large rotational basis and quadratures to converge, much larger than regularly used for other middle K_a levels. In SO_2 626 and other symmetric isotopologues, we used 0.15 Hartree (32921 cm^{-1}) for uncontracted bending functions, and 0.12 Hartree (26337 cm^{-1}) for contracted bending functions. Here they are increased to 0.35 Hartree and 0.25 Hartree, respectively. In addition, a parameter $ndimx$ was set to 25,000, which is the upper limit of the final matrix size to diagonalize, after size reduction from the original Hamiltonian matrices which range from $200\text{K} \sim 1000\text{K}$. Using this same $ndimx$ value in our early SO_2 628 calculations, convergence defects as large as $0.10 - 0.30 \text{ cm}^{-1}$ was found on some resonance-affected levels as low as $1000 - 3000 \text{ cm}^{-1}$. When $ndimx$ is increased to 40,000, most convergence defects are reduced below 0.01 cm^{-1} for levels up to 6000 cm^{-1} . The defect outliers depend on band-band interactions, vibrational quanta, energies, and J 's, etc. Generally speaking, it is always harder to ensure the full convergence of the higher energy / J states. The convergence defects of vibrational ground state levels are the easiest to locate and fix, because the CDMS data serves as a reliable reference. Note the convergence on regular levels, i.e. not affected by a resonance, are tight enough to trust levels below 6500 cm^{-1} with 0.01 cm^{-1} or better accuracy. This has been partially testified in an SO_2 626 $J=50$ test using the Ames-1B PES. The data we compared with were kindly shared from Dr. Daniel Underwood.[25,33] The fully converged, complete line list probably will require a larger $ndimx$, e.g. $80,000 - 200,000$, depending on the wavenumber range.

For this paper, most v_1 and v_3 state levels have already been converged to better than $0.01 - 0.001 \text{ cm}^{-1}$, so comparison with the new experimental observations is suitable.

New Quantum Numbers Are Available

A major improvement in this study is that the vibrational quanta and K_a/K_c “twists” issue [2] have been resolved. Now all the energy levels are reasonably labeled with the leading CI basis in the corresponding eigenvector. This improvement allows us to re-compute the published Ames-296K line lists again and provide usable and reliable quantum numbers. However, due to the very high density of states, resonances, and the non-optimal nature of the vibrational basis, these quantum numbers may not always match conventional vibrational quantum numbers reported in H_{eff} model fits. Thus, if one would like to apply a line shape parameter prediction model to our line lists to get high-lying vibrational band

line profiles, a prerequisite step is to fit our line lists with the same type of effective Hamiltonian model. The fit should probably start from band origin and low J 's, then move along progressively. It would be interesting to compare the lab-spectra based higher order spectroscopic constants vs. those fitted from our line lists. This work is being planned and will be reported in due course.

III. Results and Discussions

III.1. Comparison to CDMS data.

The CDMS database contains 11,511 SO_2 628 purely rotational transitions derived from a model fit in the $0 - 125 \text{ cm}^{-1}$ range. There are 362 experimentally measured transitions in the $0 - 36 \text{ cm}^{-1}$ range. Fig.1 (a) shows the overall comparison between CDMS and our line list: the top panel is an overview, while the bottom panel is the line position deviations in cm^{-1} and relative intensity deviations in %. Fig.1 (b) focuses on the experimental subset and gives more detailed analysis along frequency, intensity and K_a . In general, we see similar agreement for line positions as we have previously for 626 and 646, 636. For the experimental subset in Fig.1 (b), the deviations of frequency and intensity are nearly flat with respect to K_a , energy or intensities. For the expanded set in Fig.1 (a), the frequency discrepancies rapidly increase for those high J levels $>100 \text{ cm}^{-1}$ and the relative intensity deviations split into a few branches. Note our intensities were converted to 300K before comparing with the CDMS values.

Compared to 626/636/646,[2,3] the main interesting finding lies in the intensity deviations at lower energies and lower K_a 's. For example, Fig.5 of Ref.2 shows the mean intensity deviation was $<1\%$ for the 626 microwave transitions, i.e. $0.19 \pm 1.77\%$. Similar mean deviations for 646 can be found in Fig.3 of Ref.3, but Fig.5 in that same paper showed $-5 \sim -10\%$ deviations for 636. In Fig.1 (b), the relative intensity deviations are nearly uniform, distributed in a narrow range of $-9.1 \pm 0.74\%$. In Fig.1 (a), intensity deviations vary from -8% to $+5\%$, indicating the limitations of the extrapolated model. In other words, do we really have a consistency between 628 and 636, but being different from 626/646 by 10%?

The first parameter to test is the dipole moment. The effective dipole adopted in CDMS is a constant, 1.6331 D (Debye) for all three 626/636/646 isotopologues. The two components for 628 are 1.6327 D (μ_b) and 0.0328 D (μ_a). In our calculations, the identical dipole moment surface (subroutine and

coefficient data file) is used for all SO_2 isotopologue line lists. The dipole value at the potential minimum is 1.629402 D, and the experimental dipole is 1.62673 D.[34] This $\sim 0.3\%$ minor difference cannot explain the -9.1% discrepancy we find for the 628 intensity comparisons.

The second key factor is partition function. As stated before [2], the Ames-300K partition function of 626 is 1.2% larger than the CDMS-300K value. But for 628, the latest Ames-300K partition is 14005.66, nearly 10% larger than the CDMS-300K value, 12706.04! This is because the CDMS model does not include the v_2 state contributions. The v_2 level contributions were totally negligible at low temperatures. For example, at 75K, the Ames partition function is 1586.677 vs. the CDMS partition function of 1586.536. However, the weight of the v_2 population quickly increases along with the temperature. At 300K, it would match $\sim 10\%$ of the vibrational ground state partition. Consequently, the CDMS model overestimates the 300K intensities by about 10%. At 500K, it matches to more than 22% and causes similar overestimates. Thus, the $\sim -9\%$ discrepancy is clarified.

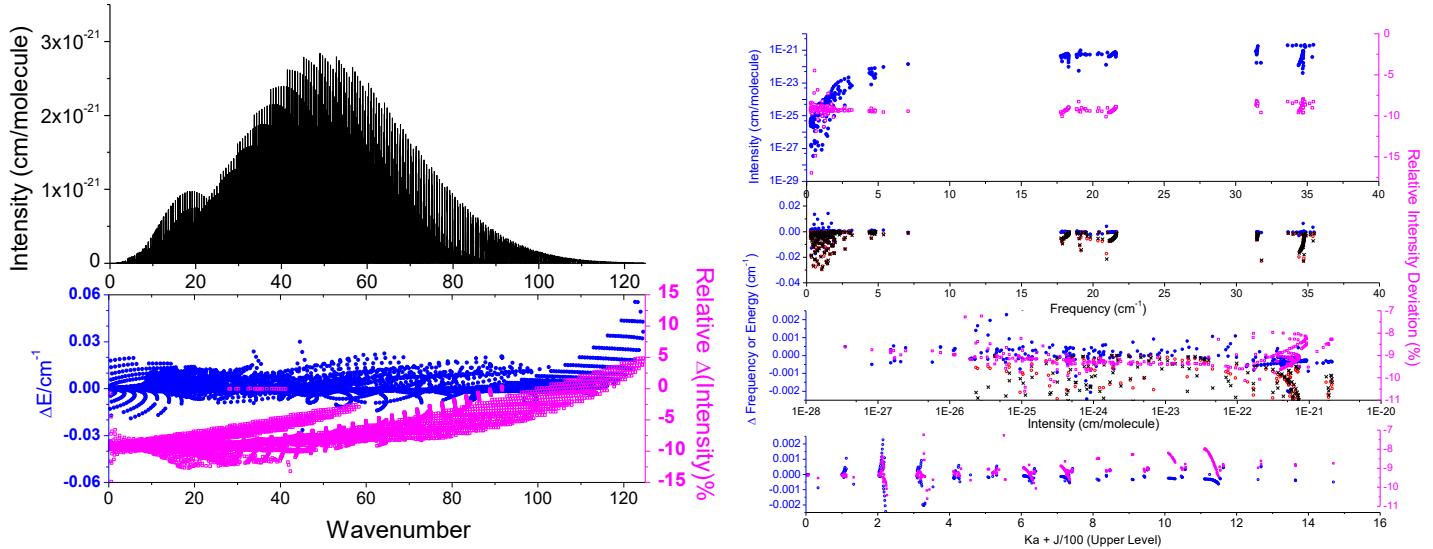


Fig.1 SO_2 628 purely rotational transitions: Ames vs. CDMS. Top left panel is the overall spectrum (black), bottom left figure shows line position deviations (blue) and relative intensity deviations (cyan) of 11,511 transitions. The 4 plots on the right side show the agreement for the 362 purely experimentally measured transitions from which the CDMS model was fit.

Now we would ask about 646: its 300K partition sums are 6614.45 (Ames) and 6020.75 (CDMS). Why does this $\sim 10\%$ discrepancy not appear in Fig.3 of Ref.3? The reason is simple: that comparison was vs. HITRAN2012, not directly vs. CDMS, and the HITRAN2012 intensities were converted from the

CDMS intensities. Details of the conversions can be found in the Appendix A of Ref.4, which includes the scaling of the partition sums. The conversion used a partition sum close to the Ames value. At 300K, the HITRAN2012 SO₂ 646 partition is 6520.897 [35], only 1.4% smaller than the Ames value. Therefore the HTIRAN2012 vs. Ames intensity differences are not really noticeable.

III.2. Ames 628 line list vs. Experiment: Overall Comparison

Ulenikov *et al* [1] reported the 628 v_1/v_3 rovibrational term values in the range of $J=0-17/18$, while their effective Hamiltonian model extended to $J=58/68$. Term values of ground state levels were not explicitly given in their paper or supplementary file. Assuming the CDMS rotational levels were adopted in their analysis, we may compare with the reported line positions, including two fundamentals v_1/v_3 and two pure-rotational hot-bands $v_1 \leftarrow v_1$ and $v_3 \leftarrow v_3$.

For asymmetric triatomics such as SO₂ 628, the $J_{J-kc,kc}$ and $J_{J+1-kc,kc}$ levels sometimes may become nearly degenerate. They belong to the same *JPS* symmetry block. For example, the ground state 50_{0,50} and 50_{1,50} levels are computed to be 721.69422508 and 721.69424382 cm⁻¹, with a 1.9E-5 cm⁻¹ separation. In addition, $J_{ka,J-ka}$ and $J_{ka,J+1-ka}$ may become nearly degenerate, too, but they have opposite parities so they do not mix. For example, the v_1 29_{18,11} and 29_{18,12} levels are computed to be 1919.36091922 cm⁻¹ and 1919.36091758 cm⁻¹, respectively. The difference is only 1.6E-6 cm⁻¹. Therefore it is natural to have many transition doublets coupled together and hard to separate one from the other in an observed spectral analysis. In the Fig.2 footnote from Ref.1, it explicitly specifies that a “*d*” symbol was used for all those $K_c=J-K_a$ and $K_c=J+1-K_a$ cases where the transition frequency differences are <0.0001 cm⁻¹. Moreover, it also included 114 $K_a=’d’$ doublets. For example, the doublet feature at 1101.9775 cm⁻¹ was marked as 35_{d,35} \leftarrow 36_{d,36}, where “*d*” refers to $K_a=0$ or $K_a=1$, not K_c . The source of this degeneracy originates from nearly degenerate levels of same parities, not opposite parities. Among the two energy level pairs, 4 transitions may arise: (all allowed by selection rules, see below):

Freq (Ames)	Intensity	Transition
1101.95945 cm ⁻¹	1.251E-21	35 _{0,35} \leftarrow 36 _{1,36}
1101.96057 cm ⁻¹	1.111E-22	35 _{0,35} \leftarrow 36 _{0,36}
1101.96099 cm ⁻¹	1.111E-22	35 _{1,35} \leftarrow 36 _{1,36}

1101.96211 cm^{-1} 1.251E-21 35_{1,35} \leftarrow 36_{0,36}

so we can see the transition pair measured and reported in Ref.1 should be one of the two pairs, $\Delta K_a=0$ or ± 1 . The 0.0027 cm^{-1} separation between the first and last transition ($\Delta K_a = \pm 1$) might not be clearly distinguished. A higher-resolution IR rovibrational measurement is required to identify these individual components. In some more extreme cases the four transitions between E' and E'' pairs may become a quartet, not only a doublet. For example, all four 53_{0/1,53} \leftarrow 52_{0/1,52} transitions are within $1149.78673 \pm 0.00001 \text{ cm}^{-1}$.

The selection rules for all 628 rovibrational bands are $\Delta J=0,\pm 1$; $\Delta K_a=0,\pm 1, \pm 2, \pm 3, \dots$; $\Delta K_c=\pm 1, \pm 3, \pm 5, \dots$, as given in Ulenikov *et al* [1]. This agrees with the selection rules built into the Ames quantum rovibrational calculations. The available transitions in Ulenikov *et al.*[1] or in CDMS have various ranges of ΔJ , ΔK_a and ΔK_c , e.g. ΔK_c extends to -5 in the CDMS data.

(1) Intensity

Ref.23 and Ref.1 did not give the exact 828/628/626 ratio for their survey spectrum, see Fig.1 in Ref.1. However, they reported that the ratio varied from 70/20/10 (beginning) to 30/30/40 (after 13.5 hrs) and ended at 15/35/50 (after 27 hrs). In other words, the 628 ratio increased from 20% to 35%, 626 from 10% to 50%, while 828 dropped from 70% to 15%. Our 1:1:1 mixed IR simulation is shown in Fig.2, using 0.001 cm^{-1} half-width for all transitions. Assuming 100% abundances, 626 has the strongest v_1 band and 628 has the weakest v_3 band. Comparing Fig. 2 to the reported survey spectrum, the 1:1:1 mixture has more 626 IR contributions in $1130 - 1170 \text{ cm}^{-1}$ range and around 1370 cm^{-1} . This suggests the actual in-situ ratio was probably not 1:1:1. The relative intensity pattern of the 828 and 626 band features suggests that the survey spectrum was taken during the first half of the 27 hours.

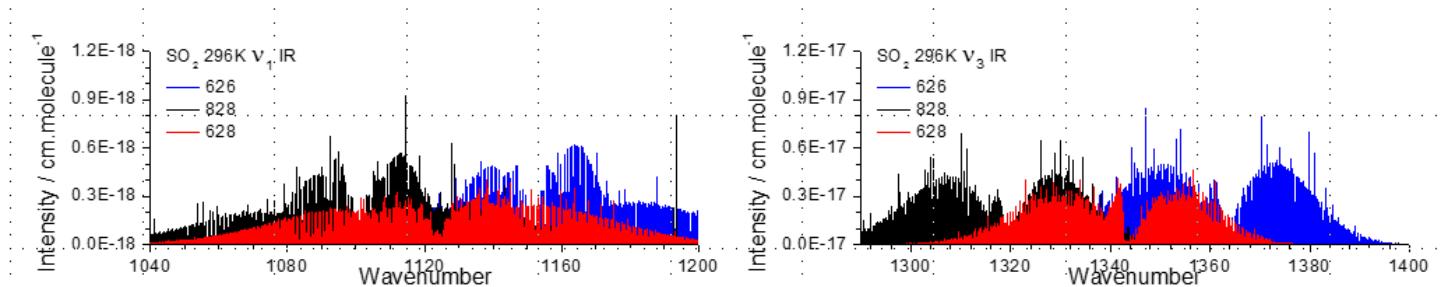


Fig.2 1:1:1 IR Spectrum of SO_2 626, 628 and 828 isotopologues using the Ames-296K line lists. Left:

v₁. Right: v₃.

On the other hand, due to very high density of transitions with similar intensities, the reported survey spectrum is not suitable for isotopologue-band specific comparisons, or in a small range. Instead, we use the assigned transitions given in the Supplementary file of Ref.1. We use (100-Transmittance)% to simulate the intensity of stick spectra, because no line shape parameters are available. Note that several typos have been identified in the Supplementary file data, and corrections are made on the J'' and K_a'' of transitions at 1322.5471 cm⁻¹, 1333.1696 cm⁻¹, 1339.4702 cm⁻¹, and 1340.4101 cm⁻¹.

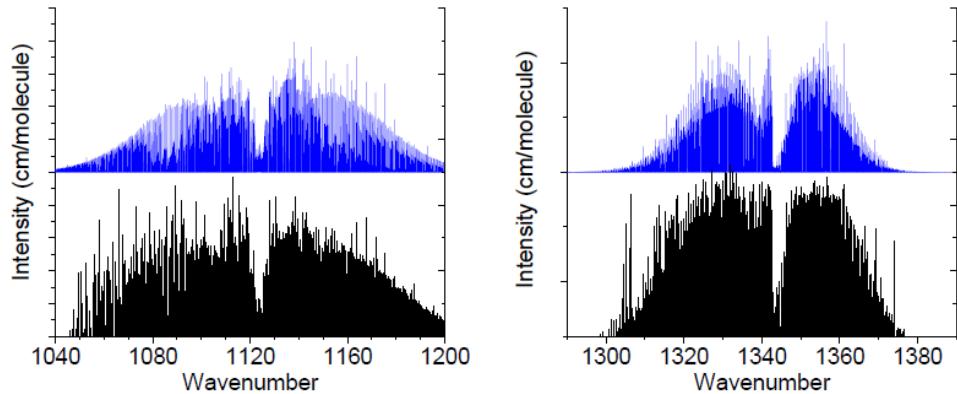


Fig.3 SO₂ 628 IR Spectrum: Ames Line List (This work) vs. Expt. (Ref.1). Left: v₁. Right: v₃. Top: Ames Line list (blue). Bottom: Transitions reported in Ref.1 supplementary file (Black)

As shown in Fig.3, obvious differences can be seen in the *P* branch of v₁ and v₃, and the right end of the *R* branch of v₃. We understand the experimental temperature was 298K, 2K higher than our list temperature, 296K. Such a 2K minor difference cannot account for these discrepancies. If there are no typos in the reported transmittance data, the most probable explanation would be the 628 and 828 lines are so close that the intensities cannot be separated. We explore this in the next section.

(2) Line positions

A few v₃ outliers have been identified and rejected from generally reasonable matches found between the reported line positions and Ames predictions. These outliers belong to the non-doublet features, i.e. there is no quantum number or selection rule confusion.

The 49_{4,45} ← 49_{4,46} assignment at 1318.4421 cm⁻¹ cannot be correct, because we have 1369.9276 cm⁻¹ of 49_{4,45} ← 48_{4,44} successfully reproduced and ground state 49_{4,46} at 764.78 cm⁻¹ matched to better than 0.02 cm⁻¹. The 49_{4,45} ← 49_{4,46} should be 1356.44 cm⁻¹, i.e. 37.83 cm⁻¹ higher. Two additional similar

cases were found: the 1360.0389 cm^{-1} feature assigned to $41_{3,39} \leftarrow 41_{3,38}$ and the 1359.1205 cm^{-1} feature assigned to $39_{3,37} \leftarrow 39_{3,36}$. Both of our computed ground state levels are confirmed by CDMS energies. For each transition, two more transitions associated with the same upper v_3 level are reproduced with agreement $\sim -0.018\text{ cm}^{-1}$. The correct frequencies should be 1325.42 cm^{-1} and 1327.22 cm^{-1} , respectively

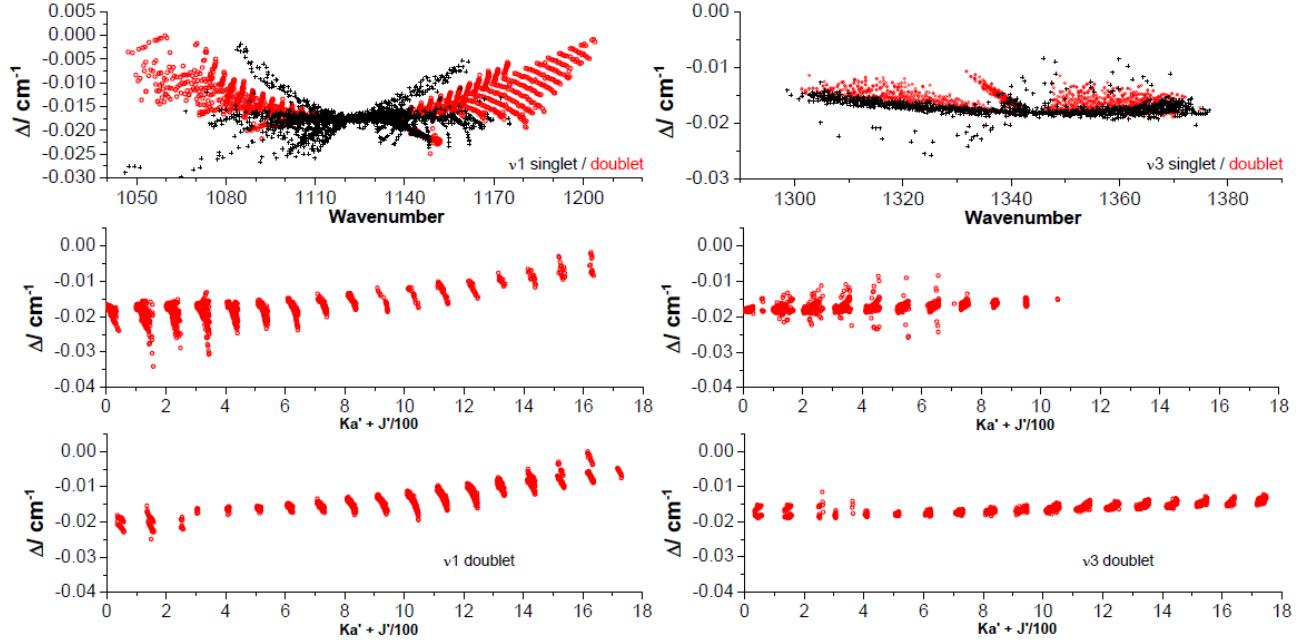


Fig.4 Line position deviations of the Ames Line list for SO_2 628. Left: v_1 . Right: v_3 . Top panel: deviations vs. wavenumbers, including doublets (red) and non-doublet transitions (black); Middle panel: singlet deviations vs. $K_a + J'/100$; bottom panel: doublet deviations vs. $K_a + J'/100$.

With these outliers excluded, the line position deviations of v_1 and v_3 are shown in Fig.4. $\Delta \pm \sigma$ (Ames – Expt) = $-0.0126 \pm 0.0039\text{ cm}^{-1}$ for v_1 , and $-0.0159 \pm 0.0014\text{ cm}^{-1}$ for v_3 . The full deviation range of double features is $-0.0249 \text{--} -0.00003\text{ cm}^{-1}$ for v_1 , and $-0.0190 \text{--} -0.0108\text{ cm}^{-1}$ for v_3 . For non-doublet transitions, the ranges are relatively wider: $-0.03412 \text{--} -0.00179\text{ cm}^{-1}$ for v_1 , and $-0.02587 \text{--} -0.00839\text{ cm}^{-1}$ for v_3 (plus two outliers at $+0.0093$ and $+0.0102\text{ cm}^{-1}$).

III.3. Ames list vs. the 2016 Expt. Paper: v_1 in three spectral windows

The extent of the agreement between the Ames list (296K) and experimental intensities (298K) is verified. A $+0.015\text{ cm}^{-1}$ blue shift is applied to our v_1 and v_3 transitions, due to the band origin deviations caused by the refinement residual left on the Ames-Pre2 PES.

For v_1 , we choose the $1160\text{--}1180\text{ cm}^{-1}$ range from the R branch. In Fig.5, the top three figures show

20 cm^{-1} , 2 cm^{-1} and 1 cm^{-1} spectral windows, respectively. The black stick spectra are measured data given in the Ref.1 supplementary file. The blue peaks are based on the Ames-296K line list. The main peaks match very well, especially the relative intensities. From the quantum mechanical calculation's point of view, this kind of agreement should indicate the reliability and consistency of both upper and lower rovibrational state wavefunctions, and the dipole moment derivatives, i.e. the curvature and shape of the dipole moment surface adopted in the intensity calculation. The *P* branch spectra intensities are based on the exact same set of wavefunctions and dipole derivatives. Therefore, the quality of our *P* branch spectra should be as reliable as the *R* branch.

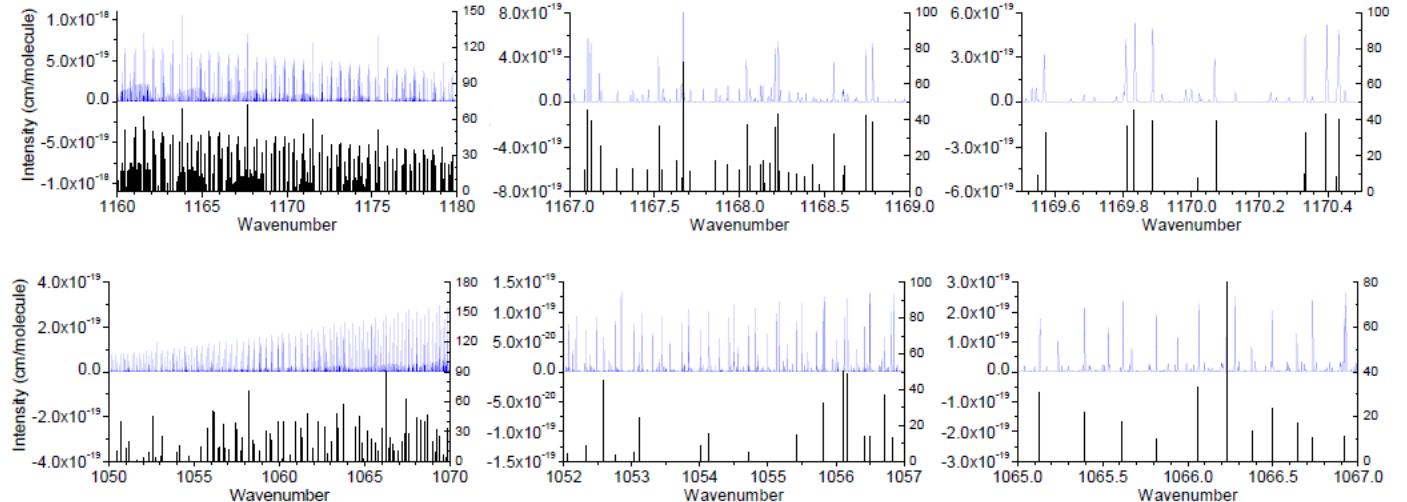


Fig.5 SO_2 628 ν_1 comparison: Ames List (purple, top panel in each plot) vs. measured transmittances reported in Ref.1 (black, bottom panel in each plot). Top three plots: *R* branch agreement in 20, 2 and 1 cm^{-1} windows. Bottom three plots: *P* branch discrepancies in 20, 5 and 2 cm^{-1} windows.

Another key observation in the top figures is that the line position deviations associated with major peaks are fairly consistent and systematic. Sometimes the relative intensity (transmittance) ratio of two strong neighboring lines with similar intensities in a doublet can be reversed when comparing the calculations with values reported in Ref.1. Given the above analysis, in these cases it is likely that the line positions are accurate and that the relative intensity of the two lines is more uncertain or in slight error. In analyzing the data, we have found no cases that are inconsistent with this assertion.

The three bottom panels in Fig.5 show the 1050 – 1070 cm^{-1} range of the weird ν_1 *R* branch. The bottom middle plot shows a 5 cm^{-1} wide range centered around 1055 cm^{-1} where a lot of computed transitions were missing from reported data. It may be that the overlap with the 828 transitions causes

extra difficulty in spectral analysis in this range, consequently many features were not assigned yet and thus are not included in the supplementary data.

The intensity irregularity is a more serious concern. As shown in the bottom left panel of Fig.5, the observed intensities have large oscillations, in contrast with the Ames list peaks (blue). These oscillations make it hard to match relative intensity patterns. For example, the reported transmittance is 69.2% for $27_{12,15/16} \leftarrow 28_{13,16/15}$ at $1065.1419 \text{ cm}^{-1}$. Its absorption is two times stronger than the transmittance of $26_{12,14/15} \leftarrow 27_{13,15/14}$ at $1065.8261 \text{ cm}^{-1}$, 90.1%. [1] In the Ames list, the two doublets should have similar intensities: $3.153\text{E-}22 \text{ cm/molecule}$ vs. $3.39\text{E-}22 \text{ cm/molecule}$, respectively.

An extreme example is shown in the bottom right panel of Fig.5, for the $30_{11,19/20} \leftarrow 31_{12,20/19}$ doublet at $1066.2402 \text{ cm}^{-1}$ (expt.). The reported transmittance is 10.3%. In the Ames-296K list, the two transitions are nearly degenerate by $1\text{E-}5 \text{ cm}^{-1}$, with $2 \times 2.866\text{E-}22 \text{ cm/molecule}$ intensities, and a stronger peak can be found at $\sim 0.048 \text{ cm}^{-1}$ to its right. The stronger feature belongs to $16_{14,2/3} \leftarrow 17_{15,3/2}$, who's intensity, $2 \times 4.47\text{E-}22 \text{ cm/molecule}$, is 56% stronger than the $30_{11,19/20} \leftarrow 31_{12,20/19}$ doublet. Unfortunately, the stronger feature was missing from the Ref.1 list of assigned transitions. In the $1065\text{--}1067 \text{ cm}^{-1}$ window, several relatively strong features were missing when compared to the Ames list.

For ν_3 , similar transmittance irregularities can be found in the tails of both the P and R branches, e.g. $1304\text{--}1307 \text{ cm}^{-1}$. Interested readers can do comparisons after downloading the Ames SO₂ 628 list from <http://huang.seti.org>.

III.4. Ames List vs. the 2016 Expt. Paper: Detailed Analysis in the 0.25 cm^{-1} window

Many SO₂ papers from the Ulenikov group [13-19,21] chose a 2 cm^{-1} window to demonstrate the quality and agreement of their recorded spectra and H_{eff} model fits. Rovibrational quantum numbers were assigned to some strong transitions. Our comparisons for those spectra exhibit very good agreement. [2,3] For the 628 case, a 0.25 cm^{-1} window is chosen from the 1340.00 cm^{-1} to 1340.25 cm^{-1} region. This is probably due to the higher density of states and thus lines. There are ~ 25 absorption features in Fig.2 of Ref.1, where some features were assigned to 626 and 828 absorptions. These recorded features and published assignments provide us a great chance to demonstrate the predictive quality of the Ames SO₂ line list for this first and most abundant asymmetric isotopologue. To make an appropriate comparison,

three Ames SO₂ isotopologue line lists need to be included with proper isotopic ratio and appropriate blue shifts for all features in a line list. The shifts of the v₃ bands adopted in our simulations are: +0.017 cm⁻¹ (628), +0.013 cm⁻¹ (828), and +0.012 cm⁻¹ (626).

As mentioned previously, Ref.1 did not specify the exact isotopic ratios in its Fig.2, except that the 628 percentage was nearly constant between 30% and 40%. The statement agreed with the description given in the 828 paper [21] that the stabilized 828/628/626 ratios were about 15%/35%/50%. We initially adopted this ratio to create a “mixed” simulation using the three individual line lists, but it turns out the reported 628 ratio was probably underestimated. The simulation curves in the Fig.6 top panel are based on Ames-296K intensities of three isotopologues, which are scaled by 1.0 × S(628), 0.5 × S(626), and 0.8 × S(828). The corresponding mixing ratio is thus 0.8/1.0/0.5, i.e. 35% / 43% / 22% for 828/628/626. Comparing our matches for major peaks, we believe the ratio should be reliable to within ±5-10%. The Fig.6 intensity axis scale may be divided by 230%, though this is not necessary because it does not affect any of the following discussion. Only the peak positions and relative intensity patterns matter. The green sticks in the Fig.6 top panel are completely based on the assigned transition list given in the Ref.1 supplementary file.

Before proceeding to agreement and discrepancy details, it is necessary to emphasize again that our comparison is fully based on the published paper and supplementary data. We have tried to identify obvious typos, but cannot determine what transitions were really missing from the H_{eff} model analysis or what assignments have been updated lately. The purpose of this section is to illustrate that variationally computed line lists can be very useful in high-resolution IR analysis, especially for a crowded spectral region.

In Fig.6, there are 26 features numbered from *a* to *z*, from left to right in increasing order of wavenumbers. Ulenikov *et al* [1] marked their assignments for 20 features, and used red triangles for two 828 features and black triangles for two 626 features. In Table 2, both the reported quantum numbers and our Ames-Pre2 based assignments/intensities are given along with the observed features, including the center line positions of the features and the transmittances. If our analysis completely agrees with Ref.1, i.e. does not give any extra information for a feature, we use “Same” in its “assignment” column,

plus the Ames-296K intensities for related transitions with 100% abundance. The “Sum” column adds up the isotopic scaled intensities of related transitions to get a value which we can compare to observed transmittances.

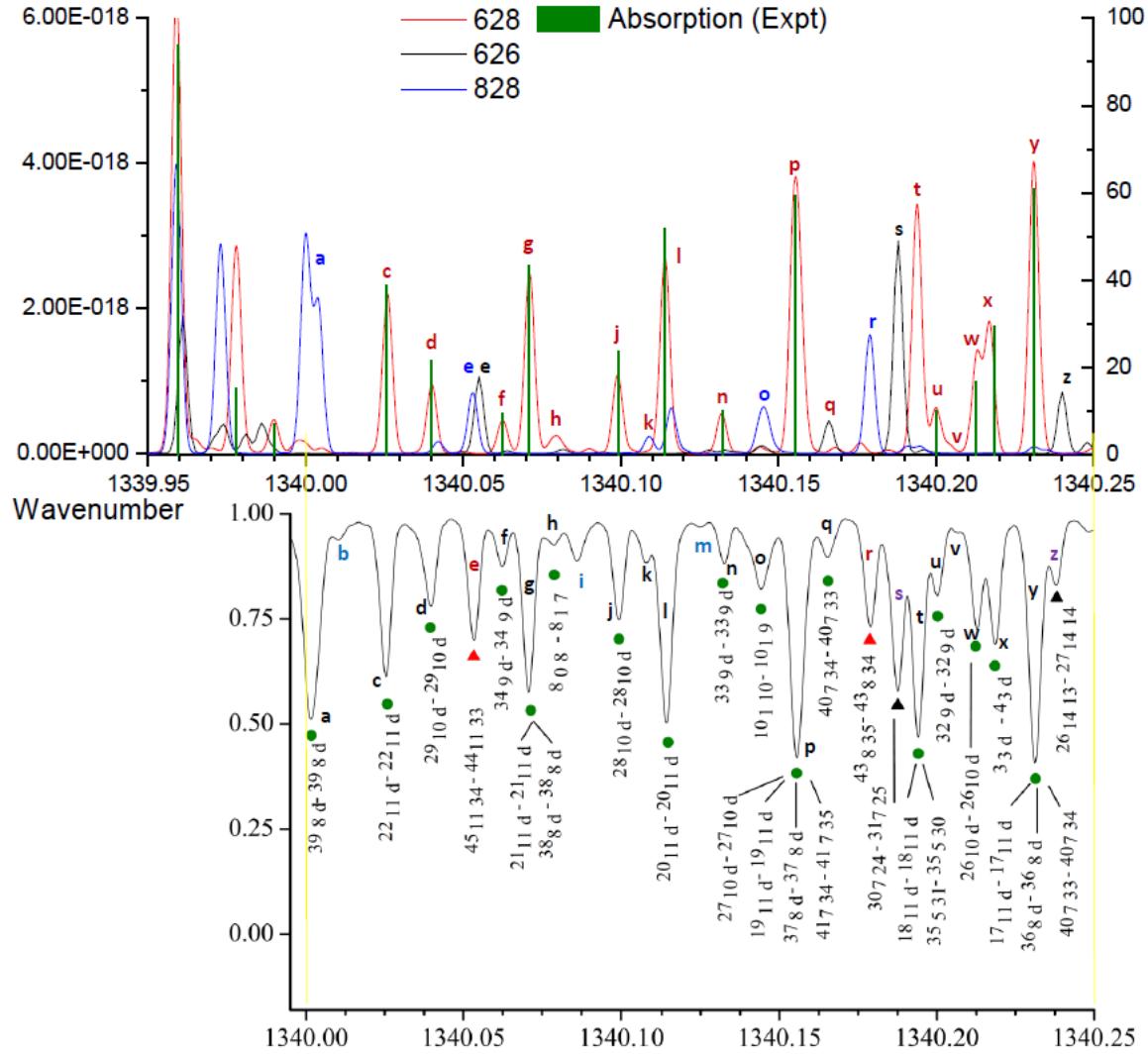


Fig.6 Ames-296K list based IR simulations (Top) vs. Experimental spectrum analysis (Bottom). Discrepancies between the Ames analysis and the reported experimental assignments are as obvious as the very good agreement. See discussion for details. $\sigma = 0.001 \text{ cm}^{-1}$ in the Ames Gaussian convolution. (The bottom figure is reproduced with permission from Ulenikov *et al.*, *J. Quant. Spectrsoc. Radiat. Trans.* 168, 29-39 (2016). Copyright 2016 Elsevier Inc.)

Here is the feature by feature analysis. “Matched” means the “Same” as the Ref.1 analysis.

(a) One may quickly notice that in the top panel the green sticks of feature *a* and *t* are missing. This is because in the Ref.1 supplementary file, we cannot find the peak $a\ 39_{8,d} \leftarrow 39_{8,d}$, or peak *t*

$18_{11,d} \leftarrow 18_{11,d}$ and $35_{5,31} \leftarrow 35_{5,30}$ assignments. Related upper level energies were not reported in Ref.1 Tables, either. Note that one of the assignments for feature g $38_{8,d} \leftarrow 38_{8,d}$ (as marked in the bottom panel) is missing from the supplementary file, too. The reported figure and the supplementary file may need synchronization.

For the two assignments in t , the Ames list has very nice matches. In addition, we can confirm that the main IR absorption is from the $18_{11,d} \leftarrow 18_{11,d}$ doublet, and the $35_{5,31} \leftarrow 35_{5,30}$ contribution is less than 3%. But for peak a , we conclude that it has to be re-assigned to two 828 transitions, $44_{1,44} \leftarrow 43_{1,43}$ (1.391E-20) and $42_{7,36} \leftarrow 41_{5,37}$ (0.972E-20). The values in parentheses are their 296K intensities predicted by the Ames list, in cm/molecule with 100% abundance. Our supporting arguments for this re-assignment include:

- (1). no strong 628 transitions can be found within $\pm 0.015 \text{ cm}^{-1}$ of 1340.00 cm^{-1} , this is a really large gap.
- (2) Ames list predicts the $628 \ 39_{8,31/32} \leftarrow 39_{8,31/32}$ doublet intensity to be $2 \times 4.14 \text{E-22}$ cm/molecule, at position $1340.000 \pm 0.002 \text{ cm}^{-1}$ (with the $+0.017 \text{ cm}^{-1}$ blue shift included). This is one order of magnitude weaker than the feature c assigned to $22_{11,d} \leftarrow 22_{11,d}$, 4.14E-21 cm/molecule. So it cannot account for the observed intensity of feature a , which is similar to that of feature c .
- (3) The two 828 transitions have intensities similar to feature c . And feature a is relatively wider than other features close by, which suggests it is the consequence of two nearby transitions, but not a doublet.

Note that the top panel of Fig.6 extends to 1339.95 cm^{-1} because we need to show that no alternative explanation or assignment works for the feature a analysis. The very strong peak at 1339.96 cm^{-1} contains observable contributions from all three species: $628 > 828 > 626$. The two features at 1339.973 cm^{-1} and 1339.977 cm^{-1} belong to $44_{1,44} \leftarrow 43_{1,43}$ (828) and two 628 doublets: $23_{11,d} \leftarrow 23_{11,d}$, $30_{10,d} \leftarrow 30_{10,d}$, respectively.

- (b) Unknown. Cannot completely rule out 628 yet.
- (c) Matched
- (d) Matched. But an 828 transition $50_{16,35} \leftarrow 49_{16,34}$ may have 15% intensity contribution.

(e) Matched

(f) Matched

(g) First assignment $21_{11,d} \leftarrow 21_{11,d}$ matched. The second one $38_{8,d} \leftarrow 38_{8,d}$ is off by $\sim 0.007 \text{ cm}^{-1}$ and intensity does not match, so probably unreliable.

(h) The original $8_{0,8} \leftarrow 8_{1,7}$ assignment cannot be the main source for this feature, because its 296K intensity $0.045\text{E-}21 \text{ cm/molecule}$ is too weak. Re-assign it to $38_{8,d} \leftarrow 38_{8,d}$.

(i) Unknown. See further discussion at the end of this section.

(j) Matched

(k) New assignment to 828 $49_{15,34} \leftarrow 48_{15,33}$. Now reasonable intensity agreement.

(l) Matched, but an 828 transition $46_{12,35} \leftarrow 45_{12,34}$ may contribute 22% intensity.

(m) Unknown. Cannot find a candidate. Might be a contamination specie or from over-populated 828 levels.

(n) Matched.

(o) The original assignment $628 10_{1,10} \leftarrow 10_{1,9}$ only contributes less than 10% of total intensity, which is even less than what 626 contributes. It is mainly an 828 feature, contributing $>80\%$ intensity: $48_{14,35} \leftarrow 47_{14,34}$ and $47_{13,34} \leftarrow 46_{13,33}$.

(p) Matched. Ames intensity predictions suggest that the $19_{11,d} \leftarrow 19_{11,d}$ and $27_{10,d} \leftarrow 27_{10,d}$ are the main sources.

(q) The original assignment $628 40_{7,34} \leftarrow 40_{7,33}$ is not strong enough to account for this feature, but the line position is okay. Re-assign to the 626 transition $25_{2,23} \leftarrow 26_{2,24}$, which is 10 times stronger than the 628 transition. Now reasonable intensity agreement.

(r) Lower state J mismatch. Could be a typo from Ref.1. “ $43_{8,35} \leftarrow 43_{8,34}$ ” has been corrected to “ $43_{8,35} \leftarrow 42_{8,34}$ ”. Now matched. In addition, about 8% intensity contribution is from 628 $16_{2,15} \leftarrow 16_{2,14}$.

(s) Lower state J mismatch. Could be a typo from Ref.1. “ $30_{7,24} \leftarrow 30_{7,25}$ ” has been corrected to “ $30_{7,24} \leftarrow 31_{7,25}$ ”. Now matched.

(t) Matched. Minor intensity contribution may arise from 828 $49_{4,45} \leftarrow 48_{4,44}$ and $50_{5,46} \leftarrow 49_{5,45}$.

(u) Matched.

(v) New Assignment. Tentatively assigned to $628 \leftarrow 294,26$. Reasonable guess and rough intensity agreement.

(w) Matched

(x) Matched

(y) Matched. Ames intensities indicate the $17_{11,d} \leftarrow 17_{11,d}$ transition is the main absorption source, yielding 87% intensity. The two 828 transitions only provide 3%.

(z) Matched.

The feature-by-feature analysis given above clearly indicate how reliable and useful the Ames line lists are. With the intensity and rovibrational quantum numbers provided at 296K, spectroscopic analysis may be significantly facilitated for regions affected by dense transitions from various isotopologues. Revisiting 628 / 828 mixture spectral analysis may be carried out soon.

In the three un-identified features b , i , and m , the most intriguing one is feature i . It is fairly strong and well separated from other features. So it is hard to mix or confuse with other potential transition candidates. While b and m could be explained by hot band lines, i is not likely a hot-band transition from either 628, 828 or 626. This is because ALL transitions were already included in our top panel simulation, and we have confidence in our prediction accuracy for both intensity and line positions of neighboring hot bands. Two possible explanations are: (1) from an unknown component, other than 626/628/828; or (2) part of the gas sample has not reached equilibrium and certain states were significantly over-populated. We are inclined to believe the first explanation was true, but not certain. We understand that the second explanation is virtually impossible, but it was first invoked by the following findings during our primitive 828 analysis. We compared the Ames 828 line list to Fig.2 of Ref.21 (828 spectra), and noticed that the intensities of some strong 828 peaks do not match well. More importantly, the footnote of that Fig.2 says “Unassigned lines probably belong to the 628 species.”, but we found this unlikely to be true. At 296K (close to the 298K experimental temperature) and in the $1292.5 - 1293.1 \text{ cm}^{-1}$ window, all 628 transition intensities are below $0.1 - 7.0 \text{E-}20 \text{ cm/molecule}$ (after Gaussian convolution), while the 828 intensities are between $0.1 - 3.5 \text{E-}18 \text{ cm/molecule}$. The 828 intensities are fifty times stronger than the 628 contributions.

At the reported 828/628 isotopic ratios: $70/20 \rightarrow 30/30 \rightarrow 15/35$, the intensity contributions from the 628 species have always been too weak to be noticed. If the 628 features are strong enough to account for the weak features in that spectra, the 828:628 ratio needs to be at least 1:5! In other words, if the “628 species” claim was valid, it suggests some absorptions could be occurring beyond equilibrium. But even with 628 features included, there still exist features that cannot be explained. Therefore, we are inclined to believe that “an unknown contamination specie(s)” is more probable for both 628 (feature *i*) and 828. Detailed comparison will be presented in our 828 paper, which will be submitted separately.

[Table 2. List of absorption features and assignments reported in Ulenikov et.al. \[Ref.1 and its supplementary file\], compared to the Ames-296K lists based, mixed IR spectral analysis \(see Fig.6\). The “Ames intensities” column values are at 296K with 100% abundance. The “Sum of Intensity” column uses a 0.35/0.42/0.22 ratio for 828/628/626 intensities.](#)

[See Table 2 at the end of text]

III.5. Other issues

The performance of the Ames 628 line list at temperatures higher than 296-300K is not the subject of this study. Based on our experience for 626 and recent convergence tests, the stability of the 628 list may sustain up to about 500-700K. We have been working extending it up to 1000K or higher, and will report this in due course.

The two microwave hot bands $v_1 \leftarrow v_1$ and $v_3 \leftarrow v_3$ reported in Ulenikov *et al.*[1] are not of key interest to this study, because they can be derived from v_1 and v_3 rovibrational levels. For the 51 $v_1 \leftarrow v_1$ transitions in the 8972 – 57,443 MHz (i.e. $0.299 – 1.916 \text{ cm}^{-1}$) range, Ames line position deviations are in the range of -54.2 – 36.35 MHz, with mean $\pm \sigma = 1.4 \pm 23.7 \text{ MHz}$, or by percentage $0.014 \pm 0.10\%$. For the 29 of 30 $v_3 \leftarrow v_3$ transitions in the 13,466 – 47,174 MHz (i.e. $0.449 – 1.574 \text{ cm}^{-1}$), Ames line positions are off by -54.0 – 23.1 MHz, with mean $\pm \sigma = 1.0 \pm 16.8 \text{ MHz}$, or by percentage $0.001 \pm 0.05\%$. An exception is $24_{3,21} \leftarrow 25_{2,24}$, where the Ames prediction is lower by -112.1 MHz.

IV. Summary and Future work

Using a new empirically refined Ames-Pre2 PES, the published *ab initio* DMS, and improved

rovibrational calculation parameters, our Ames-296K line list for SO₂ 628 is reliable and accurate enough to help and improve existing spectroscopic model analysis. In this work we compare the Ames SO₂ list to the most recent experimental spectra of the 628 v₁/v₃ bands. After the overall comparison and analysis, a few spectral windows were chosen to show both agreements and discrepancies. All the features in the 0.25 cm⁻¹ spectral window of Fig.2 of Ref.1 are carefully analyzed. By integrating the 628/828/626 line lists, we have successfully reproduced most prominent features well and identified errors or unreliable quantum numbers in Ref.1 assignments.

Our next step is to further refine the convergence of 628 rovibrational levels at higher *J* and higher energies (at least 8000 cm⁻¹). An 828 comparison paper is under preparation. Primitive 296K lists are available upon request for both 628 and 627. We need to compute Ames-296K lists for additional asymmetric isotopologue such as 648, 637, 848, etc. Additionally, we are finalizing a new cycle of PES refinement (Ames-2) and line list purification.

Size-reduced SO₂ 628 and 828 line lists for the v₁/v₃ region are available from <http://huang.seti.org>.

Acknowledgement

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Table 1. Vibrational fundamentals of 5 SO₂ isotopologues computed using the Ames-1, Ames-1B and the latest Ames-Pre2 PESs, compared to available experiments.

	v ₁	v ₂	v ₃	5v ₁
626				
Ames-1	1151.71155	517.87083	1362.05856	5682.26724
Ames-1B	1151.71382	517.87249	1362.05488	5682.17391*
Ames-Pre2	1151.70929	517.87258	1362.04648	5682.27446
Expt	1151.7130[31]	517.8726[32]	1362.0603 [31]	5682.1692 [30]
646				
Ames-1	1144.4881	513.5337	1345.08275	5647.5290
Ames-1B	1144.48729	513.53630	1345.08855	5647.41368
Ames-Pre2	1144.47592	513.53419	1345.07982	5647.51496
EXPT [28]	1144.47863	513.53871	1345.09464	
828				
Ames-1	N/A	N/A	N/A	N/A
Ames-1B	1101.13115	496.60618	1318.53466	5435.24845
Ames-Pre2	1101.13765	496.60541	1318.51958	5435.34016
EXPT [21]	1101.13648(3)		1318.54800(3)	
628				
Ames-1	1123.90994	507.37303	1342.68917	5543.83484
Ames-1B	1123.91688	507.36866	1342.80265	5543.79261
Ames-Pre2	1123.91292	507.36830	1342.79414	5543.90204
EXPT [1]	1123.930266(91)		1342.812057(94)	
627				
Ames-1	1137.77914	512.37052	1351.23491	5613.20958
Ames-1B	1137.72439	512.35916	1351.30677	5613.07476
Ames-Pre2	1137.71997	512.35897	1351.29832	5613.18002

Table 2. List of absorption features and assignments reported in Ulenikov et.al. [Ref.1 and its supplementary file], compared to the Ames-296K lists based, mixed IR spectral analysis (see Fig.6). The “Ames intensities” column values are at 296K with 100% abundance. The “Sum of Intensity” column uses a 0.35/0.42/0.22 ratio for 828/628/626 intensities.

Peak #	Peak Center	Ref.1	Ames	Ames Intensity	Intensity Sum × 10 ²⁰	Note
				cm/molecule		
	1339.959	12 _{12,d} ← 12 _{12,d}	12 _{12,d} ← 12 _{12,d} 43 _{1,42} ← 42 _{1,41} (828) 29 _{10,19} ← 30 _{10,20} (626)	1.230E-20 × 2 1.371E-20 1.342E-20	1.835	
	1339.973	n/a	44 _{1,44} ← 43 _{1,43} (828)	1.382E-20	0.484	
	1339.978	23 _{11,d} ← 23 _{11,d}	23 _{11,d} ← 23 _{11,d} 30 _{10,d} ← 30 _{10,d}	3.712E-21 × 2 1.610E-21 × 2		
	1339.990	35 _{9,d} ← 35 _{9,d}	Same	0.802E-21 × 2		
<i>a</i>	1340.002		44 _{1,44} ← 43 _{1,43} (828) 42 _{7,36} ← 41 _{7,35} (828) 39 _{8,d} ← 39 _{8,d}	1.391E-20 0.972E-20 0.414E-21	0.844	
<i>b</i>	1340.010	n/a	n/a	n/a	n/a	unknown
<i>c</i>	1340.026	22 _{11,d} ← 22 _{11,d}	Same	4.145E-21 × 2	0.348	
<i>d</i>	1340.040	29 _{10,d} ← 29 _{10,d}	29 _{10,d} ← 29 _{10,d} 50 _{16,35} ← 49 _{16,34} (828)	1.818E-21 × 2 0.757E-21	0.179	
<i>e</i>	1340.053	45 _{11,34} ← 44 _{11,33} (828)	Same	3.963E-21	0.139	
<i>f</i>	1340.062	34 _{9,d} ← 34 _{9,d}	Same	0.914E-21 × 2	0.077	
<i>g</i>	1340.071	21 _{11,d} ← 21 _{11,d}	21 _{11,d} ← 21 _{11,d} 41 _{7,35} ← 41 _{7,34} 38 _{8,d} ← 38 _{8,d}	4.626E-21 × 2 0.258E-21 0.477E-21 × 2	0.399	Suspicious
<i>h</i>	1340.079	8 _{0,8} ← 8 _{1,7}	38 _{8,d} ← 38 _{8,d} 8 _{0,8} ← 8 _{1,7}	0.477E-21 × 2 0.045E-21	0.040	
<i>i</i>	1340.086	n/a	n/a	n/a	n/a	unknown
<i>j</i>	1340.099	28 _{10,d} ← 28 _{10,d}	Same	2.048E-21 × 2	0.184	
<i>k</i>	1340.108	n/a	49 _{15,34} ← 48 _{15,33} (828)	1.094E-21	0.038	
<i>l</i>	1340.113	20 _{11,d} ← 20 _{11,d}	20 _{11,d} ← 20 _{11,d} 46 _{12,35} ← 45 _{12,34} (828)	5.158E-21 × 2 2.956E-21	0.464	
<i>m</i>	1340.124	n/a	n/a	n/a	n/a	unknown
<i>n</i>	1340.132	33 _{9,d} ← 33 _{9,d}	Same	1.041E-21 × 2	0.087	
<i>o</i>	1340.143		48 _{14,35} ← 47 _{14,34} (828) 47 _{13,34} ← 46 _{13,33} (828) 10 _{1,10} ← 10 _{1,9} 20 _{14,7} ← 21 _{14,8} (626) 12 _{1,12} ← 13 _{1,13} (626)	1.552E-21 2.162E-21 (0.1300-828) 0.348E-21 (0.0146-628) 0.426E-21 (0.0182-626) 0.107E-21	0.162 (0.0146-628) 0.107E-21	

			$19_{3,16} \leftarrow 20_{3,17}$ (626)	0.295E-21	
p	1340.155	$27_{10,d} \leftarrow 27_{10,d}$	Same	2.304E-21 $\times 2$	0.733
		$19_{11,d} \leftarrow 19_{11,d}$		5.749E-21 $\times 2$	
		$37_{8,d} \leftarrow 37_{8,d}$		0.549E-21 $\times 2$	
		$41_{7,34} \leftarrow 41_{7,35}$		0.258E-21	
q	1340.164		$25_{2,23} \leftarrow 26_{2,24}$ (626)	3.194E-21	0.083
		$40_{7,34} \leftarrow 40_{7,33}$	$40_{7,34} \leftarrow 40_{7,33}$	0.300E-21	
r	1340.178	$43_{8,35} \leftarrow 43_{8,34}$ (828)	$43_{8,35} \leftarrow 42_{8,34}$ (828)	7.763E-21	0.295
			$16_{2,15} \leftarrow 16_{2,14}$	0.547E-21	
s	1340.188	$30_{7,24} \leftarrow 30_{7,25}$ (626)	$30_{7,24} \leftarrow 31_{7,25}$ (626)	2.048E-20	0.450
t	1340.194	$18_{11,d} \leftarrow 18_{11,d}$	$18_{11,d} \leftarrow 18_{11,d}$	6.404E-21 $\times 2$	0.583
		$35_{5,31} \leftarrow 35_{5,30}$	$35_{5,31} \leftarrow 35_{5,30}$	0.328E-21	
			$49_{4,45} \leftarrow 48_{4,44}$ (828)	0.462E-21	
			$50_{5,46} \leftarrow 49_{5,45}$ (828)	0.452E-21	
u	1340.199	$32_{9,d} \leftarrow 32_{9,d}$	Same	1.183E-21 $\times 2$	0.099
v	1340.207	n/a	$29_{4,26} \leftarrow 29_{4,25}$	0.460E-21	0.019
w	1340.212	$26_{10,d} \leftarrow 26_{10,d}$	Same	2.587E-21 $\times 2$	0.217
x	1340.218	$3_{3,d} \leftarrow 4_{3,d}$	Same	3.398E-21 $\times 2$	0.285
y	1340.231	$17_{11,d} \leftarrow 17_{11,d}$	$17_{11,d} \leftarrow 17_{11,d}$	7.136E-21 $\times 2$	0.687
		$36_{8,d} \leftarrow 36_{8,d}$	$36_{8,d} \leftarrow 36_{8,d}$	0.630E-21 $\times 2$	
		$40_{7,33} \leftarrow 40_{7,34}$	$40_{7,33} \leftarrow 40_{7,34}$	0.301E-21	
			$50_{6,45} \leftarrow 49_{6,44}$ (828)	0.412E-21	(0.022)-828
			$52_{9,44} \leftarrow 51_{9,43}$ (828)	0.224E-21	
z	1340.238	$26_{14,13} \leftarrow 27_{14,14}$ (626)	Same	5.904E-21	0.130

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